PREPARATION AND CHARACTERISATION OF 60mol% Al_2O_3 & 40mol%ZrO_2 MICROCOMPOSITE BY SOL-GEL PRECIPITATION ROUTE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
Metallurgical & Materials Engineering

By

DIWAKAR KUMAR
&
SIVANANDA SUBUDHI

Department of Metallurgical and Materials Engineering
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Under the Guidance of

Prof. R.C. Behera

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NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

CERTIFICATE

This is to certify that the thesis entitled "**PREPARATION AND CHARACTERISATION OF 60mol% Al_2O_3 & 40mol%ZrO_2 MICROCOMPOSITE BY SOL-GEL PRECIPITATION ROUTE** " submitted by **Mr Sivananda Subudhi [roll no. 10304011] and Mr Diwakar Kumar [roll no. 10304034]** in partial fulfillment of the requirements for the award of **Bachelor of technology** degree in **Metallurgical & Materials engineering** at the **National Institute of Technology Rourkela** (deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge the matter embodied in the thesis has not been submitted to any other university/institute for the award of any degree or diploma.

Date: 01.05.07

Prof. R.C. BEHERA
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ACKNOWLEDGEMENT

We would like to express out gratitude towards all the people who have contributed their precious time and effort to help us. Without whom it would not have been possible for us to understand and complete the project.

We would like to thank Prof R.C. Behera, Department of Metallurgical & Materials Engineering my Project Supervisor for his guidance, support, motivation and encouragement through out the period this work was carried out. His readiness for consultation at all times, his educative comments, his concern and assistance even with practical things have been invaluable.

We are grateful to Prof. G.S. Agarwal *Head of the Dept. of Metallurgical & Materials Engineering* for providing necessary facilities in the department.

Date: 01.05.07 **DIWAKAR KUMAR [10304034]**

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ABSTRACT

A material having two or more distinct constituent materials or phases such that the integrated material has properties noticeably different from constituents is a composite material. For example in alumina-zirconia ceramic composite system, the incorporation of α-Al_2O_3 into stabilized zirconia changes the properties drastically. Ceramic materials traditionally have properties of high compressive strength, high wear resistance, high abrasion resistance and the ability to withstand high temperatures.

But one major drawback with ceramic materials is their poor toughness. Zirconia, as a ceramic material, possess remarkable properties such as high melting point, inertness to chemicals, high hardness etc. It has an added advantage that when retained in the tetragonal form in the product during use it gets transformed to monoclinic zirconia and during this process of conversion it increases the toughness of the material- the process known as transformation toughening. This unique property of zirconia can also be used to improve the properties of other ceramic materials like alumina spinel, mullite etc.

Transformation toughening is one of the best methods of improving the fracture toughness and strength of brittle ceramic materials. The stability of tetragonal zirconia phase (t-ZrO_2) is the main concern in these systems as it determines the stress required for the transformation and thus the resulting toughening achieved. Various combinations of constituent ceramic materials are taken such as Zirconia alumina, Zirconia spinel, Zirconia silicon carbide, Zirconia mullite etc.

Objective of our work is to synthesize composite having 60mol% Al_2O_3 and 40mol% ZrO_2 by sol-gel precipitation route. We are adopting this process because the distribution of the ZrO_2 particles must be uniform and the size should be slightly lower than the critical diameter at which spontaneous transformation takes place. Before starting this work, a thorough study has been made on the theory, mechanism and the research done by various authors. We have

discussed the theory and mechanism of transformation toughening. If the crystal can be restrained from undergoing martensitic transformation during cooling from high temperature by the constraint imposed by the matrix, it can be considered in a metastable state. Should the elastic constraint be removed, as would be the case ahead of the tip in a propagating crack, then the crystal could transform, the shear strain developed would oppose the growth of the crack; it is this effect which is used to advantage in transformation toughening.

In our project work we have prepared Alumina powder samples. For this we have adopted sol-gel precipitation route. In this process we have Zirconium oxy chloride and ammonium nitride salt for preparation of powder. From the salts clear solution is prepared. Then gel is formed by addition of ammonia solution which is 50% dilute. This gel is dried in an oven drier. After drying the sample is ground to obtain powder. This dried powder is subjected to calcination at different temperatures starting from 300°C to 1000°C. Then the calcined powders are taken for phase analysis by XRD.

We have observed presence of cubic phase in the temperature range of 600°C to 800°C. The disadvantage of cubic phase is that it makes the material prone to fracture. The strength of the sample increases but the toughness is very less. The cubic phase of zirconia is retained in the refractory material where very high strength is required. The tetragonal phase is observed in the temperature range of 800C to 1000°C.This tetragonal phase present in sample, while use transforms into monoclinic phase so the toughness of the material is increased. This process is known as “Transformation Toughening”. The monoclinic phase is generally unstable hence stabilizers a re required. It improves the toughness of the sample.

INTRODUCTION

A material having two or more distinct constituent materials or phases such that the integrated material has properties noticeably different from constituents is a composite material. For example in alumina-zirconia ceramic composite system, the incorporation of α-Al_2O_3 into stabilized zirconia changes the properties drastically. Ceramic materials traditionally have properties of high compressive strength, high wear resistance, high abrasion resistance and the ability to withstand high temperatures. But one major drawback with ceramic materials is their poor toughness. Zirconia, as a ceramic material, possess remarkable properties such as high melting point, inertness to chemicals, high hardness etc. It has an added advantage that when retained in the tetragonal form in the product during use it gets transformed to monoclinic zirconia and during this process of conversion it increases the toughness of the material- the process known as transformation toughening. This unique property of zirconia can also be used to improve the properties of other ceramic materials like alumina spinel, mullite etc.

Transformation toughening is one of the best methods of improving the fracture toughness and strength of brittle ceramic materials. The stability of tetragonal zirconia phase (t-ZrO_2) is the main concern in these systems as it determines the stress required for the transformation and thus the resulting toughening achieved. Various combinations of constituent ceramic materials are taken such as Zirconia alumina, Zirconia spinel, Zirconia silicon carbide, Zirconia mullite etc.

BACKGROUND

A lot of work has been done in the last thirty years to incorporate Zirconia in alumina in certain quantities such as 5mol%, 10mol, 15mol%, 20mol%, 30mol%, 50mol% of zirconia in alumina and study the densification and toughness. The majority of work has taken the respective salts as the precursor material and co-precipitated the alumina-zirconia composite from salt solution through sol-gel method. The composite has been dried, calcined, compacted and sintered to get final product. The product has been tested for various properties including toughness.

OBJECTIVE

Objective of our work is to synthesize composite having 60mol% Al_2O_3 and 40mol% ZrO_2 by sol-gel precipitation route. We are adopting this process because the distribution of the ZrO_2 particles must be uniform and the size should be slightly lower than the critical diameter at which spontaneous transformation takes place. Before starting this work, a thorough study has been made on the theory, mechanism and the research done by various authors. The present report describes this study in various chapters. In the first chapter we have discussed the theory and mechanism of transformation toughening. In this chapter we have covered various reasons and the advantages of transformation toughening. In the next chapter we have discussed the various techniques for preparation of micro composite. Various works that has been done in this field previously such as powder synthesis and transformation behavior during fracture, effect of powder treatment on crystallization behavior etc has been discussed in the next chapter.

THEORY

STRUCTURE OF ZIRCONIA

Zirconia exhibits three well-defined polymorphs. They are:-

- Monoclinic phase
- Tetragonal phase
- Cubic phase

The monoclinic phase is stable up to 1170^{o}C where it transforms to the tetragonal phase, which is stable up to 2370^{o}C where as the cubic phase up to the melting point of 2680^{o}C.

MONOCLINIC:

The Zr^{+4} ions have seven-fold co-ordination with the oxygen ions with the co-ordination nearly tetrahedral, one angle in the structure differing significantly from the tetragonal value. The structure of the oxygen ions is not therefore planar and a buckling in the O-I plane occurs. And the O-I plane is quite irregular.

TETRAGONAL:

In its tetragonal form the Zr^{+4} ions enjoy eight fold co-ordinations, there again being a distortion due to four of the oxygen ions being at a distance of 2.065 A^{o} in the form of a flattened tetrahedron and four at 2.455 A^{o} in an elongated tetrahedron rotated through 90^{o}.

CUBIC:

The high temperature cubic structure has face-centered CaF_2 structure with each Zr^{+4} ions having eight fold symmetry with the oxygen ions, which are arranged in two equal tetrahedral.

[Variation in crystal lattice and density of the three phases]

Crystal Structure	**Monoclinic**	**Tetragonal**	**Cubic**
	a=5.156	a=5.094	a=5.124
	b=5.191	c=5.177	
	c=5.304		
Density	5830 kg/m^3	6100 kg/m^3	6090 kg/m^3

STABILIZATION OF ZIRCONIA

The large volume expansion during transformation from tetragonal to monoclinic phase results in crack formation and hence leads to failure of the component during cooling. Or in other words the component is rendered unsuitable for structural applications. The stabilizers often used are MgO, CaO, CeO, Y2O3 and as a result the high temperature cubic phase becomes stable at room temperature. Thus the deleterious effects of volume expansion during transformation from tetragonal to monoclinic phase can be avoided altogether. The solubility depends on atomic radius because of high coordination number and irregular crystallography of the zirconia phase involved. Also lack of solid solubility, high vapour pressure etc. limit the range of elements to rare earth elements. Yttria and ceria can be used for high value added ceramics but it becomes uneconomical for mass market and hence inexpensive materials like MgO, CaO, etc. are used. If the amount of stabilized oxide is insufficient then it leads to partially stabilized zirconia rather than a fully stabilized form. The PSZ is usually composed of two intimately mixed phases, the cubic solid solution and the tetragonal phase and on cooling the tetragonal phase may transform to monoclinic phase.

Also it has been found that if the particle size is very small, the tetragonal phase can be retained at room temperature without the addition of any stabilizer. For retaining this metastable tetragonal zirconia the particle size should be $\leq 300A^{o}$. Or in other words there exists a critical particle size above which it will undergo phase transformation either spontaneously or with the application of stress but below it, it will not.

From thermodynamic point view it can be explained in terms of activation energy barrier and driving force. If the particle size is large the activation energy required for the transformation to take place is very low and also the process is associated with a decrease in the free energy or in other words there exists a positive driving force. Hence the transformation takes place easily. On the other hand in case of small particles there is very little decrease in free energy and the activation energy barrier is high. Thus the particle is not able to transform easily. But, in between there exists an intermediate particle size for which the barrier is low, It is accompanied by decrease in free energy and hence small but finite amount of energy is required for the transformation to take place. It has been found that the critical grain size is also dependent on the amount of stabilizer added and the degree of mechanical constraint.

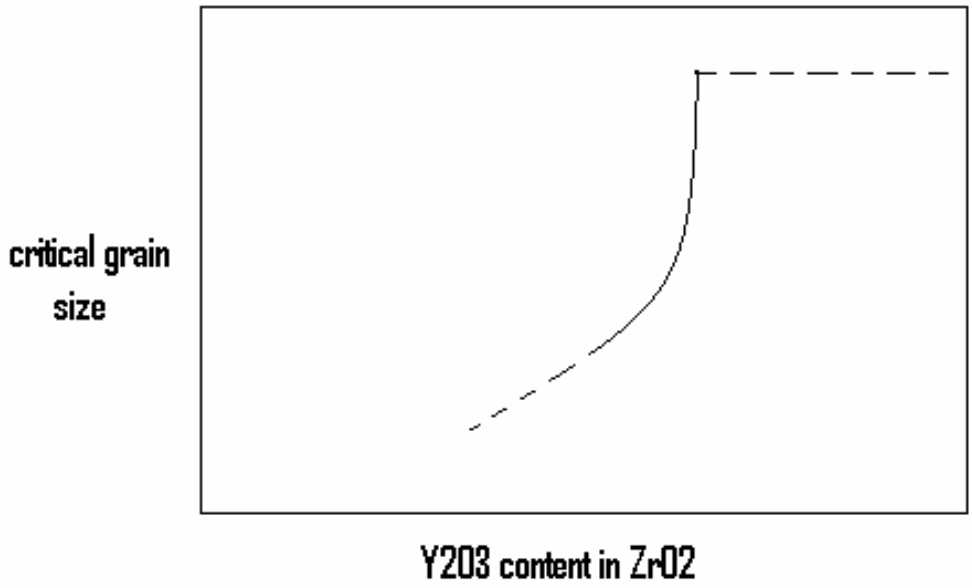


Figure 1: Dependence of the critical grain size on yitttria content

Stabilization is carried out due to reasons:

1. The volume expansion associated with the transformation from tetragonal to monoclinic during cooling may often result in large deformation which may exceed elastic and fracture limits even at relatively fine grain size.
2. On the other hand the volume expansion can be used to improve both the toughness and strength of the ceramics. When t-ZrO2 is retained in the ceramic product, the stress induced transformation produces toughened ceramics which can be used for structural applications.

The phases present, their amount, size distribution will have a profound influence on a whole range of material properties. It is the development of properties by an understanding of and ability to engineer the microstructure that has generated considerable interest in zirconia in recent years.

TYPES OF STABILIZED ZIRCONIA

Depending on the types and amount of phases present, there are basically three types of stabilized zirconia:-

1. Partially stabilized zirconia (PSZ)
2. Tetragonal zirconia polycrystals (TZP)
3. Fully stabilized zirconia (FSZ)

Partially stabilized zirconia:-

Stabilizers like MgO, CaO etc. are used to obtain partially stabilized zirconia. PSZ is a mixture of monoclinic, tetragonal and cubic phases. The following conditions are to be met to prepare PSZ:-

- The concentration of the dopant oxide should be less than that needed for producing fully stabilized zirconia.
- The cubic phases should be heat treated so as to obtain a two phase mixture.

Tetragonal zirconia polycrystals:-

These ceramics consist of 100% tetragonal phase. These ceramics are dense, fine grained and stabilized by yittria and other rare earths. Here addition of stabilizer is done along with heat treatment.

Fully stabilized zirconia:-

These are also called cubi9c stabilized zirconia (CSZ).The concentration of dopant oxide should b sufficient so that the matrix is completely cubic and it is stable from room temperature up to melting point. It can be obtained by addition of CaO, MgO, CeO, Y2O3 etc.

TRANSFORMATION TOUGHENING

The transformation from cubic to tetragonal and that from tetragonal to monoclinic is martensitic in nature. The transformation is characterized by the fallowing properties:-

- The composition of the transformed phase is same as the parent phase.
- As it is diffusion less transformation certain crystallographic planes and directions within the parent phase will be common in the product.
- Transformation takes place with sonic velocity.
- It is a thermal type that is transformation continues with decrease in temperature and no transformation take place at constant temperature.
- Transformation takes place with small atomic displacement.

If the crystal can be restrained from undergoing martensitic transformation during cooling from high temperature by the constraint imposed by the matrix, it can be considered in a metastable state. Should the elastic constraint be removed, as would be the case ahead of the tip in a propagating crack, then the crystal could transform, the shear strain developed would oppose the growth of the crack; it is this effect which is used to advantage in transformation toughening.

Zirconia can be used for increasing both the strength and toughness of ceramics by utilizing the tetragonal to monoclinic phase transformation of metastable tetragonal particle induced by the presence of the stress field ahead of the crack. The volume change and shear strain developed in the martensitic reaction oppose the opening of the crack and therefore act to increase the resistance of the ceramics to crack propagation.

It is generally recognized that apart from crack deflection which can occur in two phase ceramics, the tetragonal to monoclinic transformation can develop significantly improved properties by two different mechanisms.

MICROCRACKING

The toughening can be achieved by incorporating ZrO2 particles in the ceramic matrix, such as Al2O3. These zirconia particles undergo transformation from tetragonal to monoclinic phase and undergo 3 to 5 %volume expansion. The tangential stresses around the zirconia particles lead to micro crack formation around it. These cracks have the ability to expand in the field of the propagating crack or to defect the propagating crack. This enables to absorb or dissipate the energy of the crack and thereby improves the fracture toughness of the ceramic material.

The size of the zirconia particles should be such that it undergoes transformation but at the same time the size of the cracks produced around the transformed zirconia particles should not be very large. Controlling the milling time prior to sintering or ageing time after sintering can control the size of the particles. An optimum level of volume fraction ensures maximum toughness. If this level is increased then the micro cracks interact with one another resulting in decrease in strength. Such microstructures are useful in resisting thermal shock conditions.

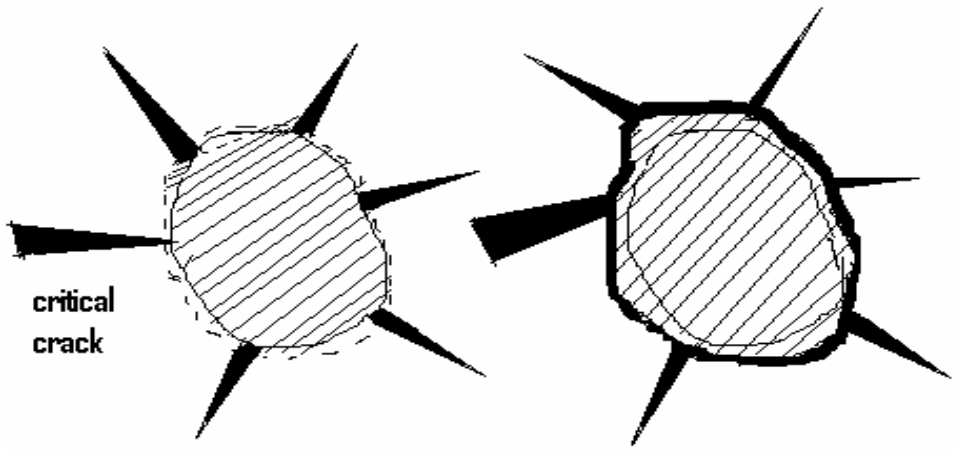


Figure 2: The martensitic transformation that occurs in ZrO2 with its 3-5% volume expansion develops micro cracks around the ZrO2 particles. A crack propagating into the particles is deviated and becomes bifurcated thus increasing the measured fracture resistance.

There are two conditions. The first is the resistance to the initiation of fracture by thermal shock. This is given by

$$R=\sigma/\alpha E$$

Where, σ = fracture stress

α = thermal expansion coefficient

E = elastic modulus

R^1 may be increased by increasing σ or decreasing α and E. The practice it has been found possible to alter all three parameters beneficially. The second parameter R^{11} is considered to be the resistance to growth of pre-existing flaw, by a thermal stress, given by

$$R^{11} = \sqrt{(E_\gamma / 2\ \sigma^2)}$$

STRESS INDUCED TRANSFORMATION TOUGHENING

The zirconia particles can be introduced into the matrix as second phase particles or can be developed by heat treatment. These particles are finely divided and a constraining force is exerted on them by the matrix. Hence the transformation does not occur. If a crack is made to extend, large tensile stresses are generated around the crack especially ahead of the crack tip. These tensile stresses release the constraint exerted by the matrix on the tetragonal zirconia particles and if sufficiently large can result in a net tensile stress on the particles, which will transform to monoclinic zirconia. The volume expansion (>3%) and shear strain (1-7%) developed in the particle causes the martensitic reaction, with a resultant compressive strain generated in the matrix. Since this occurs in the vicinity of the crack; extra work would be required to move the crack through the ceramic accounting for the increase in toughness and hence strength.

This phenomenon requires a critical particle size to be effective. If it is smaller then there will be no transformation and if it is larger then it will undergo phase change spontaneously. This critical size depends on the matrix constraint and composition of zirconia. As the cubic stabilizing oxide content increases, the chemical free energy associated with the transformation decreases and hence larger particles can be induced to remain in metastable tetragonal form.

The critical particle sizes for constrained and unconstrained conditions are given as follows;

For unconstrained condition:

$$r = -3(\Delta\sigma) / q\,(1-T/T^{1})$$

Where,

$\Delta\sigma$ = change in surface free energy between the high temperature phase and the low temperature phase

r = critical particle radius

q = heat transformation per unit volume of n infinite crystal

T^{1}= transformation temperature of an infinite crystal

For constrained conditions

$$r = 6(\gamma_m - g_s\gamma_t) / (|\Delta G| - \Delta U_{se})$$

γ_m and γ_t are the interfacial surface energies in the monoclinic and tetragonal states, g_s is the ratio of the interfacial surface areas of the two phases, ΔG is the free energy of the system and ΔU_{se} is the strain energy associated with the transformed particle.

COMPRESSIVE SURFACE LAYERS

Thus transformation toughening can be used not only to increase the strength of the ceramics but also the ceramics become less sensitive to surface cracks formed. The zirconia based transformation toughened ceramics develop compressive surface layers because of the spontaneous transformation of the zirconia particles near the surface because of the absence of the hydrostatic constraint near the surface. Surface grinding can be employed so that the compressive stresses penetrate to a grater depth and thereby lead to toughening.

The development of a compressive surface layer makes the material, less sensitive to small surface defects, which might be introduced while handling or during use. Any small abrasion less than the critical flaw size, introduced into the surface is immediately placed into compressive, the abrasive flaw being effectively removed

From its possible role as critical flaw….

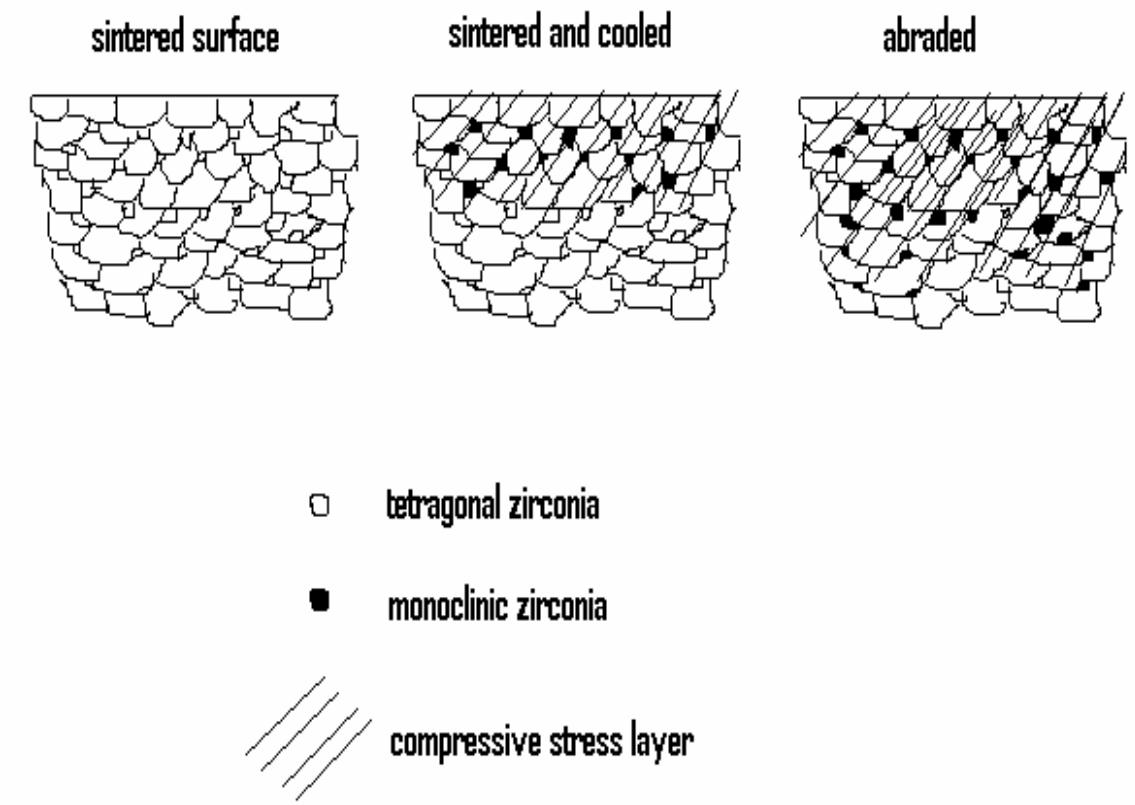


Figure 3: Diagram of a section through a free surface at

(a) The sintering temperature. On cooling, particles of ZrO2 near the surface

(b) Transformation due to reduced constraint, developing a compressive stress in the matrix. The thickness of this compressively stressed layer can be increased (c) by abrasion or machining.

APPLICATION

The properties of zirconia ceramics outlined earlier suggest that the combination of strength, toughness and chemical resistance should allow application of the materials in harsh environments under severe loading conditions. In conjunction with the development of a surface compressively stressed layer many novel applications in wear resistant and cutting devices are envisaged. The alumina-zirconia ceramics have superior strength, toughness and wear resistance when compared to conventional alumina and consequently the composite ceramic has found use as a cutting tool tip. Alumina-zirconia abrasion wheels outperform the pure alumina variety by a factor of 8.

Many cutting applications have been found, items such as scissors and shears have proved particularly successful for the cutting of difficult materials such as Kevlar, outlasting conventional tool steels. Cutting applications have also been found in the kitchen, the paper industry and in hair salons, where clipper blades have been found to be advantageous due to their corrosion resistance. For economic reasons this class of materials is being investigated for internal combustion engine components. Seals, particularly where combinations of wear resistance and corrosion resistance is required, offer possibilities for this type of material.

TECHNIQUE FOR PREPARATION OF MICROCOMPOSITE

There are several methods for the preparation of alumina zirconia powders.

- **Conventional route: -** The conventional methods involve either dry milling or wet milling the mixture of available alumina and zirconia powders but this results in inhomogeneous mixing in terms of particle spacing and non uniform ceramic microstructure. A modification includes use of aqueous slurry for the purpose. A new approach involves controlling the pH of the slurry and the slip casting it in a gypsum mold.

- **Electrophoretic deposition: -** A homogenous, well dispersed solution with the ions having identical charge polarity and electrophoric mobility is used to produce alternating electrophoretic depositions of Al2O3 and ZrO2.

- **Alumina-zirconia powders with corrugated microstructures: -** They are prepared from viscous non-polar suspensions of alumina and zirconia powders. Two alumina and one zirconia layers of 1mm thickness are stacked and rolled together to form 1mm thick laminates, which are then repeatedly folded and rolled, each time with a 50% reduction in thickness. ZrO2-Al2O3 eutectic plates produced by laser zone melting:-it involves preparing large surfaces of eutectic composites directionally solidified, from the melt, with very fine uniform microstructures. Large surface plates of the Al2O3-ZrO2 eutectic with thickness up to 250μm can be grown by solidification using a modified laser zone melting method suitable for the preparation of large area samples. The surface of a ceramic precursor is scanned with CO2 laser beam, which induces surface melting.

- **Mixture of fuels approach for solution combination synthesis of Al2O3-ZrO2 nanocomposites:-** Appropriate fuels when properly mixed proportions upon combination will give Al2O3-ZrO2 nanocomposite. Here nano size particles can be produced.

An increase in volume fraction of zirconia beyond 20 to 30% shows a decline in properties with increasing tendency towards coarsening and reduced tetragonal retention. The deterioration in properties is due to non-uniform distribution and agglomeration of ZrO2 particles resulting in larger particles and reduced tetragonal content. However if agglomeration and coarsening of ZrO2 particles can be prevented through some improved processing, a significant increase in composite toughness results even at ZrO2 content beyond 30%. Producing the matrix by sol-gel precipitation route can increase volume percentage of zirconia.

WORK PREVIOUSLY DONE

A lot of work has been done in the last thirty years to incorporate Zirconia into alumina in certain quantities such as 5mol%, 10mol, 15mol%, 20mol%, 30mol%, 50mol% of zirconia in alumina and study the densification and toughness.

The majority of work has taken the respective salts as the precursor material and co-precipitated the alumina-zirconia composite from salt solution through sol-gel method. The composite has been dried, calcined, compacted and sintered to get final product. The product has been tested for various properties including toughness. The previous works include

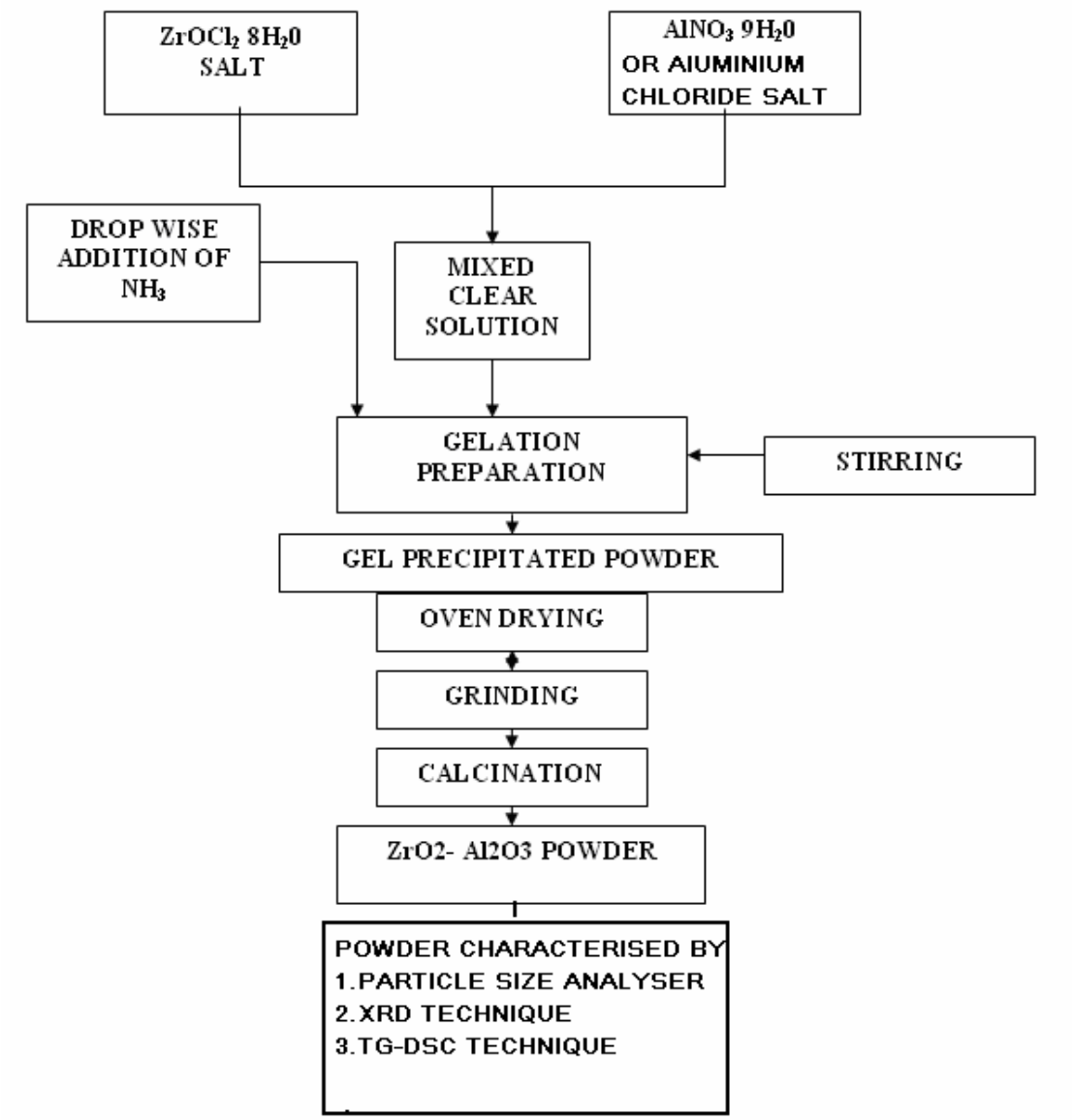
- Preparation and characterization of an Al_2O_3- ZrO_2 nanocomposite
- Effect of powder treatment on the Crystallization behavior and phase evolution of Al_2O_3- high ZrO_2 nanocomposite
- Ultrasonic velocity measurements in Al_2O_3- ZrO_2 ceramic composite system
- Phase distribution and residual stresses in the melt-grown Al_2O_3- ZrO_2 eutectics
- Grain size control and phase transformation in nanophase Al_2O_3- ZrO_2

Objective of our work is to synthesize composite having 60mol% Al_2O_3 and 40mol% ZrO_2 by sol-gel precipitation route.

OUTLINE OF THE PROJECT WORK DONE

- ***SOLUTION PREPARATION***
- ***GEL PREPARATION***
- ***DRYING OF GEL***
- ***GRINDING OF DRIED GEL***
- ***THERMAL ANALYSIS OF POWDER (TG & DSC)***
- ***CALCINATION OF POWDER AT DIFFERENT TEMPERATURES (300°C TO 1000°C)***
- ***XRD ANALYSIS OF POWDERS***
  (CALCINED AT DIFFERENT TEMPERATURES)

FLOW DIAGRAM FOR PROCESSING OF Al_2O_3- ZrO_2 POWDER



EXPERIMENTAL DETAILS

INSTUMENTS AND TECHNIQUES

The following instruments were used for preparation of samples and for their testing

1. X-Ray diffractometer
2. Electrically heated chamber type furnace
3. Simultaneous thermal analyzer
4. Magnetic stirrer
5. Drying oven

X-RAY DIFFRACTOMETER

This is an instrument for studying crystalline (non-crystalline) materials by analysis of the X-ray intensity peaks and d value at a particular wave length.

Instrument Specification:

Target used: Cu target
Wavelength: 1.54 A°
Power: 30 KV, 20 mA
Range of observation: 10° - 90°
Rate: 2°/min

ANODE	*FILTER*
Copper	Nickel
Cobalt	Iron
Chromium	Vanadium
Molybdenum	Zrconium

PARTICLE SIZE ANNALYZER

Master micro manufactured by Malvern Instrument is fully computer controlled and runs through windows software. This can measure the particle size from 0.05 – 550 micron. Accurate and repeatable results depend on the type of sample and the dispersion agents used. For better dispersion three mechanisms are used simultaneously: stirring, ultrasonic & chemical agent. Mastersizer Micro includes a powerful ultrasonic probe, variable pump speed and ultrasonic timer. Samples can be measured directly from a standard laboratory beaker. There is a syringe option for small volumes of emulsion which injects the sample directly into the measurement cell. Alternatively the proven Mastersizer small volume sample dispersion unit can be used as an accessory.

ELECTRICALLY HEATED CHAMBER TYPE FURNACE

This is electrically heated chamber type furnace using silicon carbide heating elements (spiral type), maximum temperature up to 1500 C and working at 1400-1500. It is accompanied with a digital PID programmable controller and thyristor power drive.

The size of heating cavity: 6” 5” 15”

Power: 3phase 10KW (approx)

Thermocouple: Pt-Pt/Rh 10% is also provided in the furnace

SIMULTANEOUS THERMAL ANALYSER

Thermal analysis is a series of technique that study the effect of temperature on material properties, functioning simultaneously for analysis by differential scanning calorimetry. Differential scanning calorimetry (DSC) and thermo-gravimetry(TG) have proved themselves particularly suitable for research and quality control applications in

industrial and university environment. TG measures any change in weight of sample with its surrounding atmosphere as a function of temperature. The DTA/DSC technique measures enthalpy changes and reaction temperature during physical transition and chemical reaction. Either the temperature difference (DTA) between the sample and reference or the heat flux difference (DSC) is determined. The results of both techniques can be directly compared as reaction equilibrium are not affected by differing the sample atmosphere which can occur with single measurement. In addition the thermal effects measured in this way are easier to interpret and enthalpy changes can be corrected for weight change. More over, STA is able to eliminate the uncertainty and geometry of samples and in accuracy in the temperature.

MAGNETIC STIRRER

It is used to mix the solution homogeneously. The stirring action in the solution is caused by the movement of magnetic bar in the solution. The magnetic bar is placed in beaker. It is moved by magnetic stirrer.

HEATING OVEN

The oven is used for drying purposes. Ii is an electrically heated oven. Inside the oven there is a fan to maintain the uniform temperature in the dryer and makes heat transfer rapid. It removes moisture from samples. It can operate up to a maximum temperature limit of 300.

POWDER PREPARATION:

As for the project requirement we have prepared 10 batches of powder where each batch weighed 1.5 grams of powder. All batches are 60-40 weight of Al_2O_3-ZrO_2 powder mixture.

CHEMICALS REQUIRED*:*

The chemicals required for the production of gel and subsequently into powder are given below.

The specifications of chemicals are:

1. Zirconium Oxychloride ($ZrOCl_2$.12.H2O)
   95% chemically pure
2. Aluminium Nitride ($Al(NO_3)_3.9H_2O$)
   95% chemically pure
3. Ammonia solution
   50% dilute
4. Distilled Water

SOLUTION PREPARATION

Two solutions are prepared from two salts $ZrOCl_2$.$12H_2O$& Al $(NO_3)_3.9H_2O$ salts with distilled water. As per the stoichiometric requirement $ZrOCl_2$ powder & Al $(NO_3)_3.9H_2O$ powder are taken. The weighed amount of $ZrOCl_2.12H_2O$ & Al $(NO_3)_3.9H_2O$ is added in measured quantity. Then the solution is mixed by magnetic stirrer.

CALCULATION:

Preparation of 100 grams of 60-40 weight% of alumina-zirconia powder:

102 grams of Al2O3 from 2×375 grams of Al(NO3)3.9H2O

60 grams of Al2O3 from 2×375×60/102 grams

= 441.17 grams of Al(NO3)3.9H2O

- Purity = 95%
- So actual amount of Al(NO3)3.9H2O required

  = 441.17/0.95 = **464.39 grams**

123.22 grams of ZrO_2 from 322.22 grams of $ZrOCl_2.8H_2O$

40 grams of ZrO_2 from $322 \times 40/123$ grams

= 104.60 grams of $ZrOCl_2.8H_2O$

- Purity = 95%
- So total amount of $ZrOCl_2.8H_2O$ required

= 104.60/ 0.95 = **110.10 grams**

GEL PREPARATION

For the preparation of gel as per the stoichiometric requirement the solution is prepared. The mixed solution is kept in beaker. The beaker is placed on the magnetic stirrer and the stirring of the solution is carried out by magnetic spin bar. Then ammonia is added drop wise from a burette. Due to addition of ammonia, precipitation takes place initially and subsequently gel is formed. At the end of gelation an excess amount of ammonia is added.

DRYING GEL

The prepared gel is dried in oven for 48 hours at 95°C. After completion of drying the gel is removed from oven and cooled.

GRINDING OF GEL

The dried gel is ground in the agate. The gel is subjected to phase analysis by XRD and TGDSC test.

CALCINATION OF GEL:

The gel is calcined to obtain ZrO_2-Al_2O_3 powder. During calcination zirconia hydroxide and aluminium hydroxide converted into ZrO_2-Al_2O_3 powder. The calcination temperature is determined from TG/DSC. The calcination is also carried out at different temperatures starting from 300°C to 1000°C to find out the phase changes taking place in zirconia when heated. Then the calcined samples are subjected to XRD for phase analysis.

RESULTS & DISCUSSION

XRD OF DRIED GEL:

The X-ray diffraction pattern of the gel dried at 90°C is shown in the [fig no 05]. The XRD pattern does not have any sharp peak for crystallization phases; however it has one or two peak which is typical of amorphous material. The XRD pattern indicates that dried gel is amorphous having no crystalline phases. The superimposed peaks are identified to be NH_4Cl which is a result of the reaction between liberated HCL and NH_4OH.

THERMAL ANALYSIS OF DRIED GEL:

The samples were calcined at different temperatures starting from 300°C to 1000°C at 10°/min rate of heating. The thermal analysis (DSC and TG curves) of the dried gel powder are presented in fig No 06. The similarity in the decomposition behavior of the gels is remarkable. For all the gels the decomposition reactions (measured through weight loss) have taken place in three places in three broad steps covering almost same temperature ranges. The DSC curve also shows similar characteristic features with minor changes in peak value with change in composition. At low temperature, up to just above 100°C, there is a gradual weight loss associated with loss of excess water in the gel. There is a corresponding endothermic feature on the DSC curves around 100°C demonstrating it is a decomposition reaction. The second stage of weight loss starts from about 200°C and extends up to 300° C. This step is probably associated with the decomposition reactions involving un-reacted $ZrOCl_2$. Finally there is another weight loss starting from about 375°C and extending up to 400°C. This weight loss does not have a corresponding endothermic peak in any of gels.

This weight loss may be due to NH_4Cl evaporation or evolution of water of crystallization. However, at higher mole % of Al_2O_3, a clear exothermic peak for crystallization of Al_2O_3 could be seen. Thus it appears that addition of Al_2O_3 delays the crystallization reaction and it shifts towards higher temperature. However the TG/DSC plot indicates that the major decomposition reaction is complete in the temperature range of 800°C. Thus the calcination temperature will be decided on the basis of maximum tetragonal and cubic phase formed. It is expected that at this temperature all the decomposition reaction will be completed and crystallization will just start. Since the decomposition reactions are diffusion controlled, long holding time was given to ensure the completion of all the decomposition reactions.

XRD OF CALCINED POWDER:

Upon calcination hydroxides Zr $(OH)_2$ & Al_2O_3 converted to oxides(ZrO_2- Al_2O_3). The dried gels are calcined at different temperatures ranging from 300°C to 1000°C for 8 hours. X-Ray diffraction pattern of gel powder calcined from 300°C to 1000°C for 8 hours are shown in fig no 07 to 14. The X-Ray indicates that the material is totally amorphous at 300°C & 400°C. The XRD powder calcined at 500°C [fig no-9] indicates that the material is still largely amorphous. The crystallinity has just started appearing. Right from the beginning when crystallinity starts it is cubic phase only. The XRD powder calcined at 600°C [fig no-10] shows that the degree of crystallinity (cubic) has increased. The XRD powder calcined at 700°C [fig no-11] shows that only cubic phase is present. The XRD powder calcined at 800°C [fig no- 12] indicates that tetragonal phase of zirconia has started forming. The XRD powder calcined at 900°C [fig no-13] indicates that more amount of tetragonal phase is also present. Hence right from the beginning when crystallinity starts it is cubic phase only. From 800°C onwards tetragonal zirconia is found to be formed and from 1000°C onwards monoclinic zirconia will be formed.

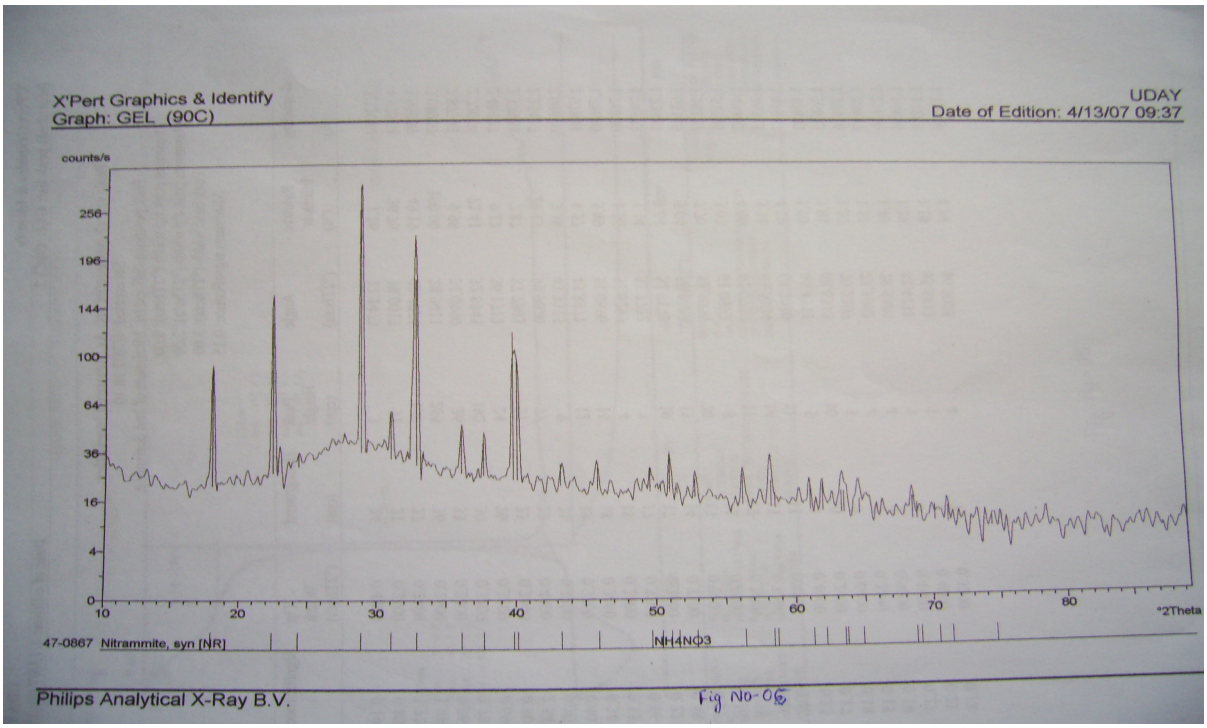

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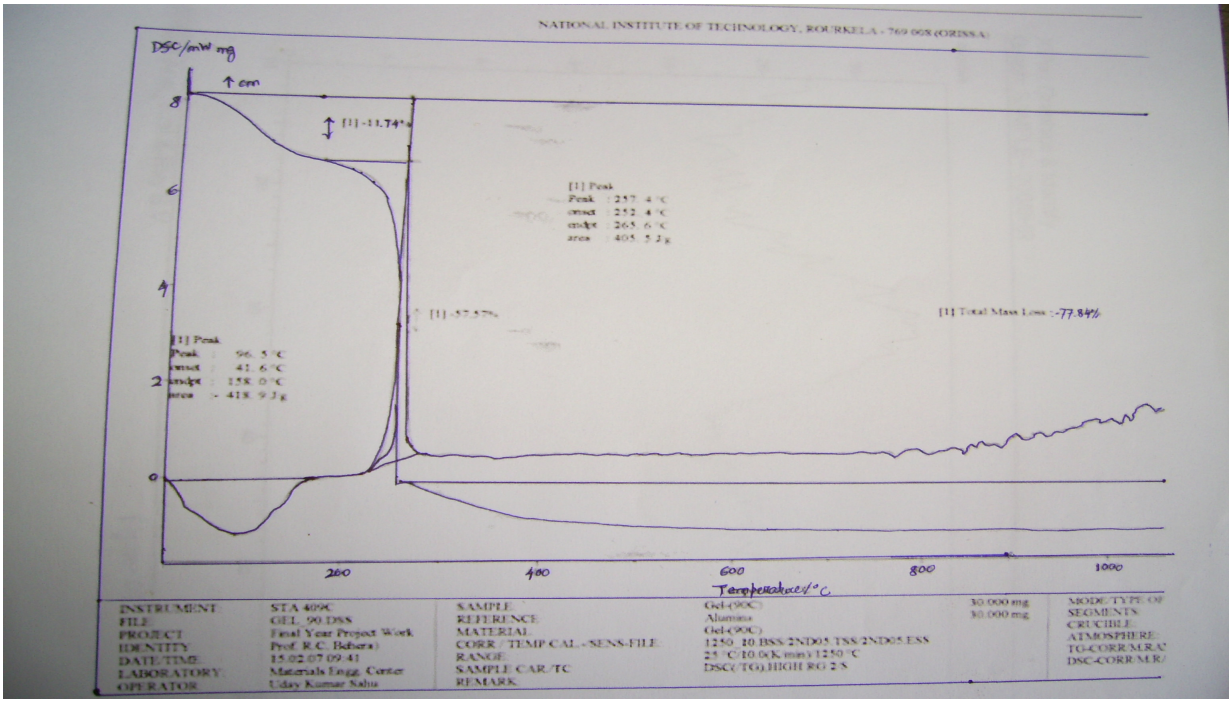
Fig No-05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[1] Peak
Peak : 257.4 °C
onset : 252.4 °C
endpt : 265.6 °C
area : 405.5 J/g
[1] -57.57%
[1] Total Mass Loss : -77.84%
[1] Peak
Peak : 96.5 °C
onset : 41.6 °C
endpt : 158.0 °C
area : -418.9 J/g
200
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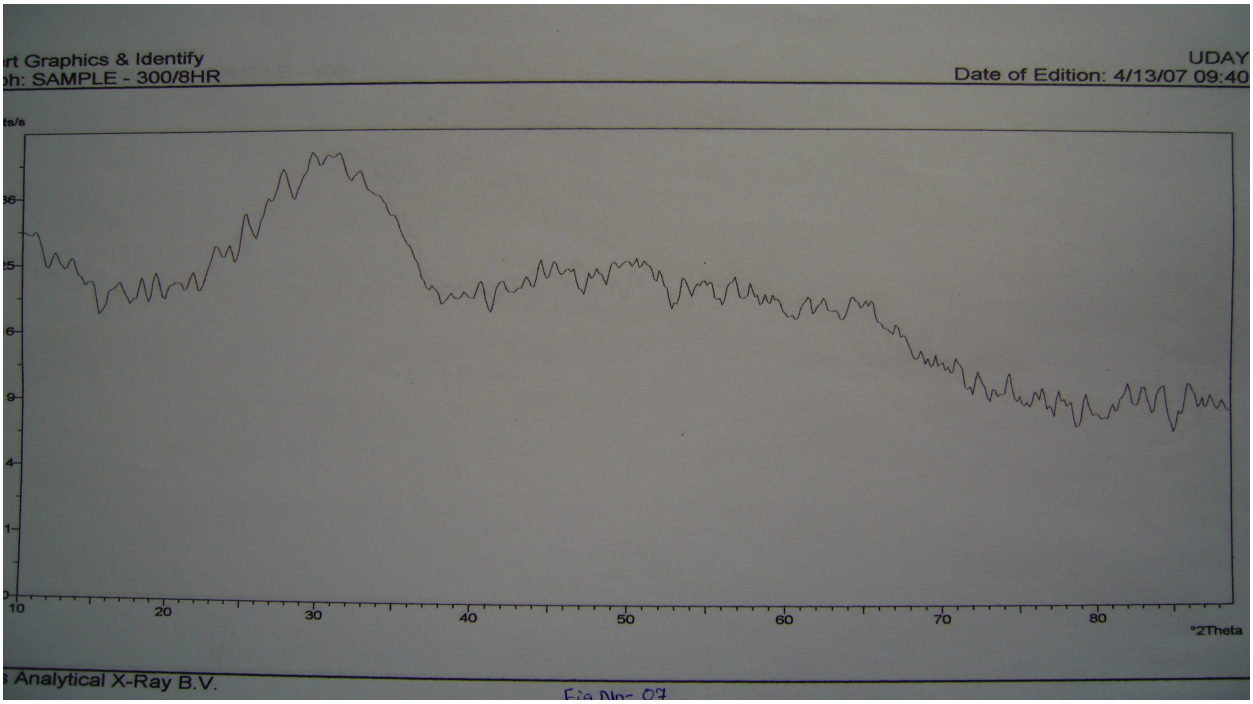
Temperature/°C
INSTRUMENT: STA 409C
FILE: GEL_90.DSX
PROJECT: Final Year Project Work
IDENTITY: Prof. R.C. Behera
DATE/TIME: 15.02.07 09:41
LABORATORY: Materials Engg. Center
OPERATOR: Uday Kumar Sahu
SAMPLE: Gel-(90C)
REFERENCE: Alumina
MATERIAL: Gel-(90C)
CORR. / TEMP.CAL.-SENS-FILE: 1250_10.BSS-2ND05_TSS-2ND05.ESS
RANGE: 25 °C/10.0(K/min)/1250 °C
SAMPLE CAR./TC: DSC(TG),HIGH RG 2 S
REMARK:
30.000 mg
30.000 mg
MODE/TYPE/OF SEGMENTS:
CRUCIBLE:
ATMOSPHERE:
TG-CORR.M.R.:
DSC-CORR.M.R.: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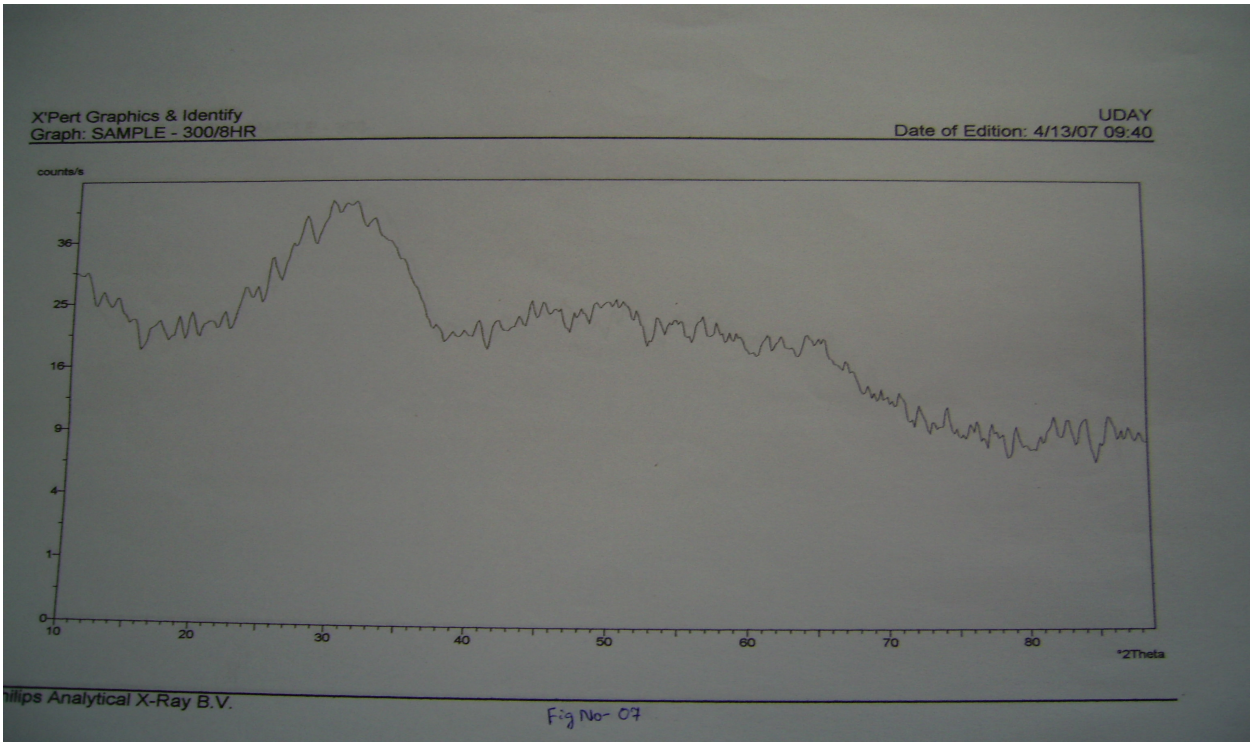
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Fig No- 07

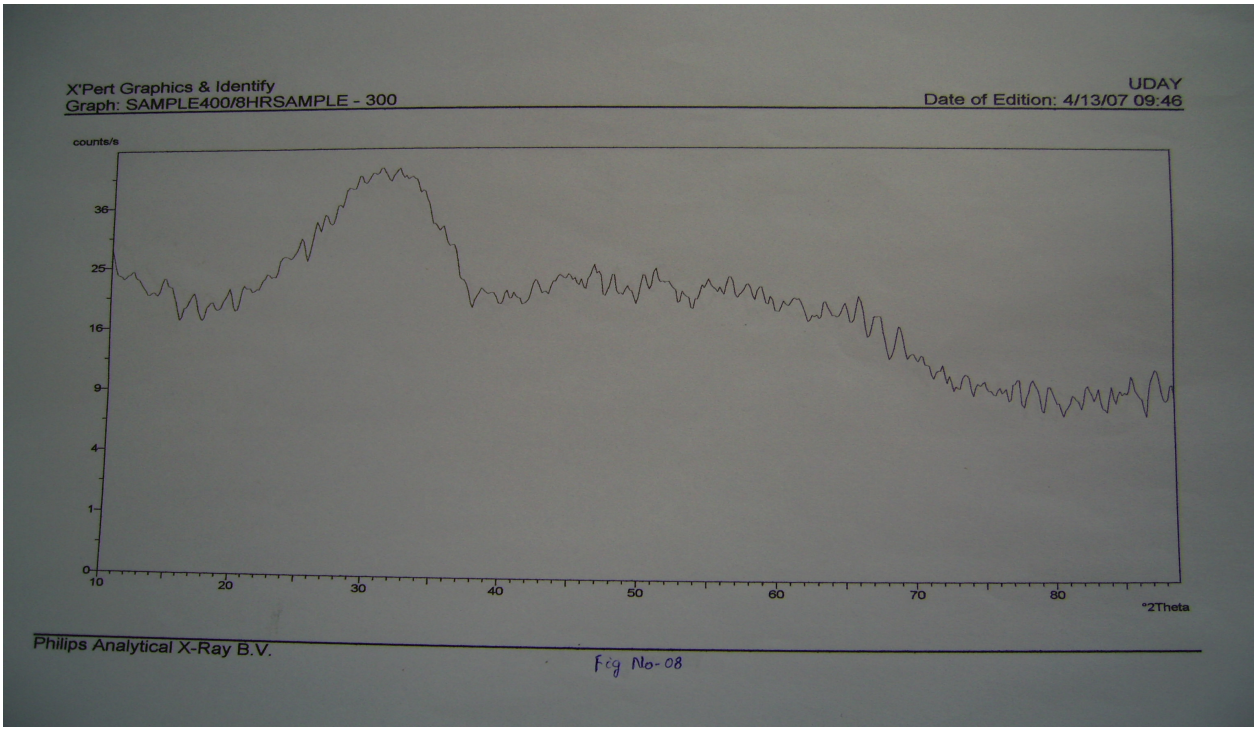


Fig No-08

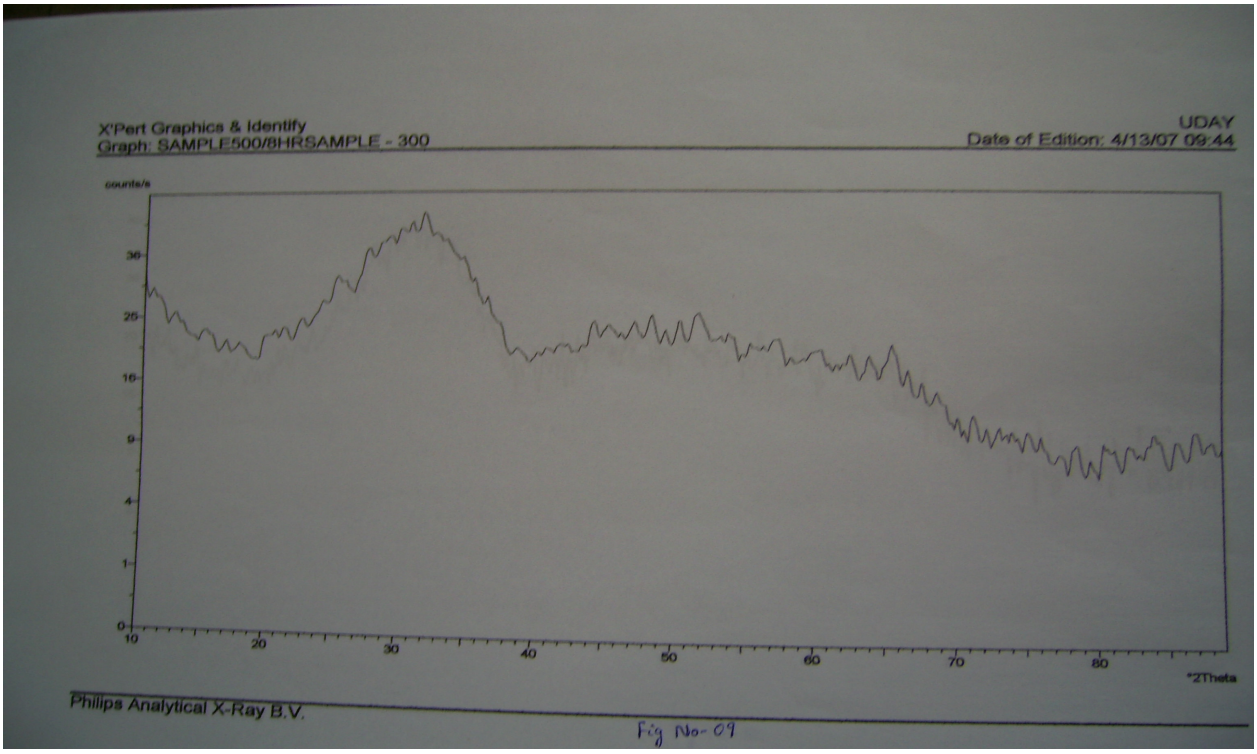


Fig No-09

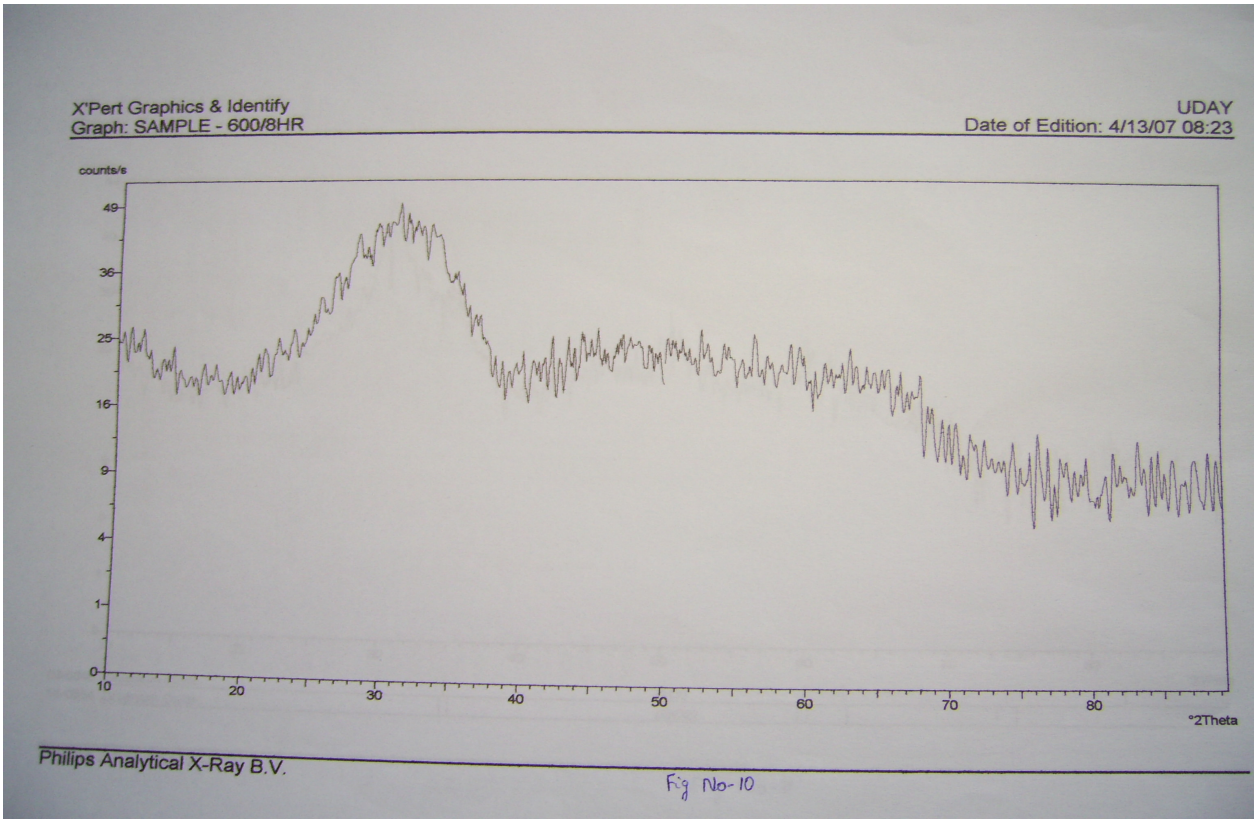


Fig No-10

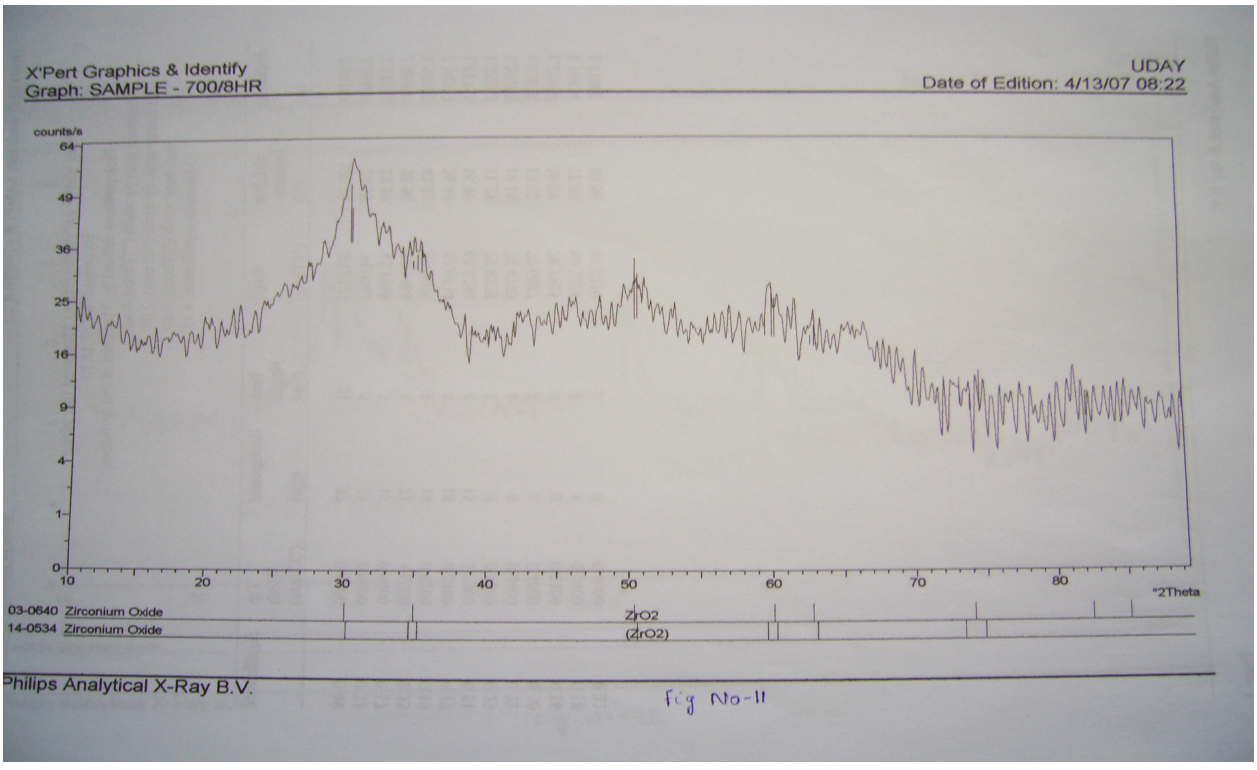


Fig No-11

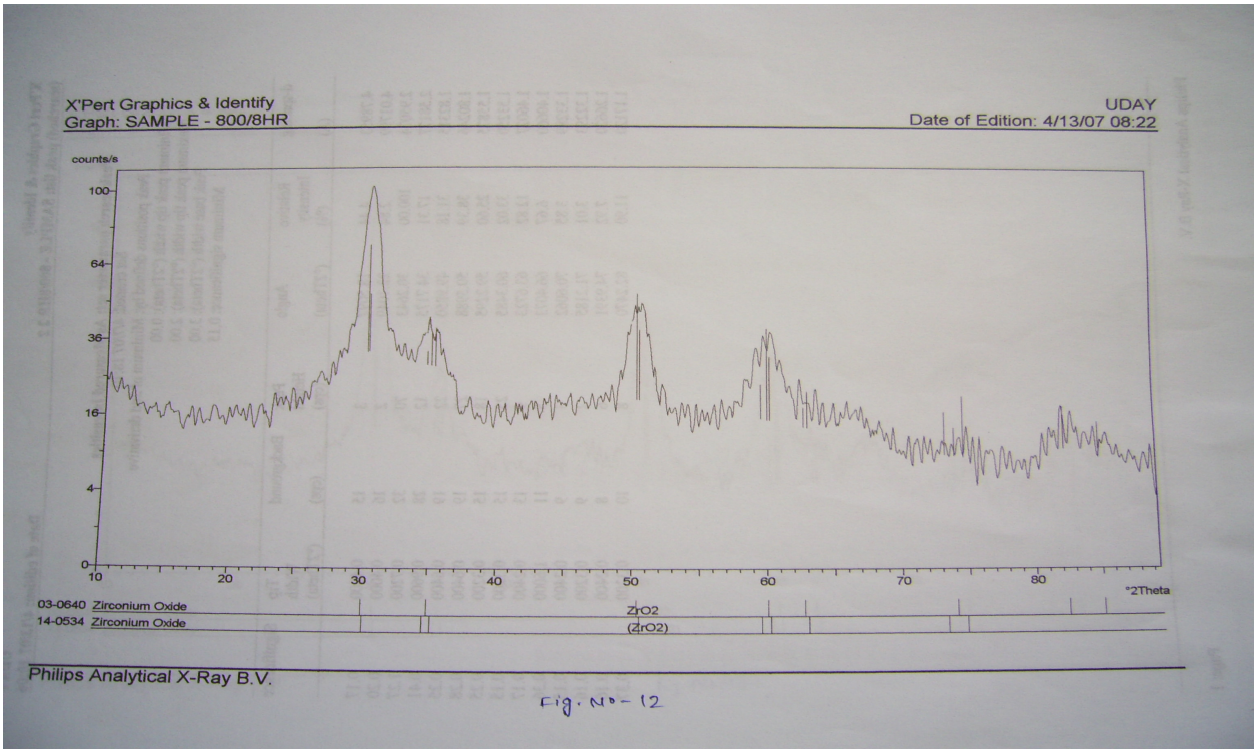


Fig. No - 12

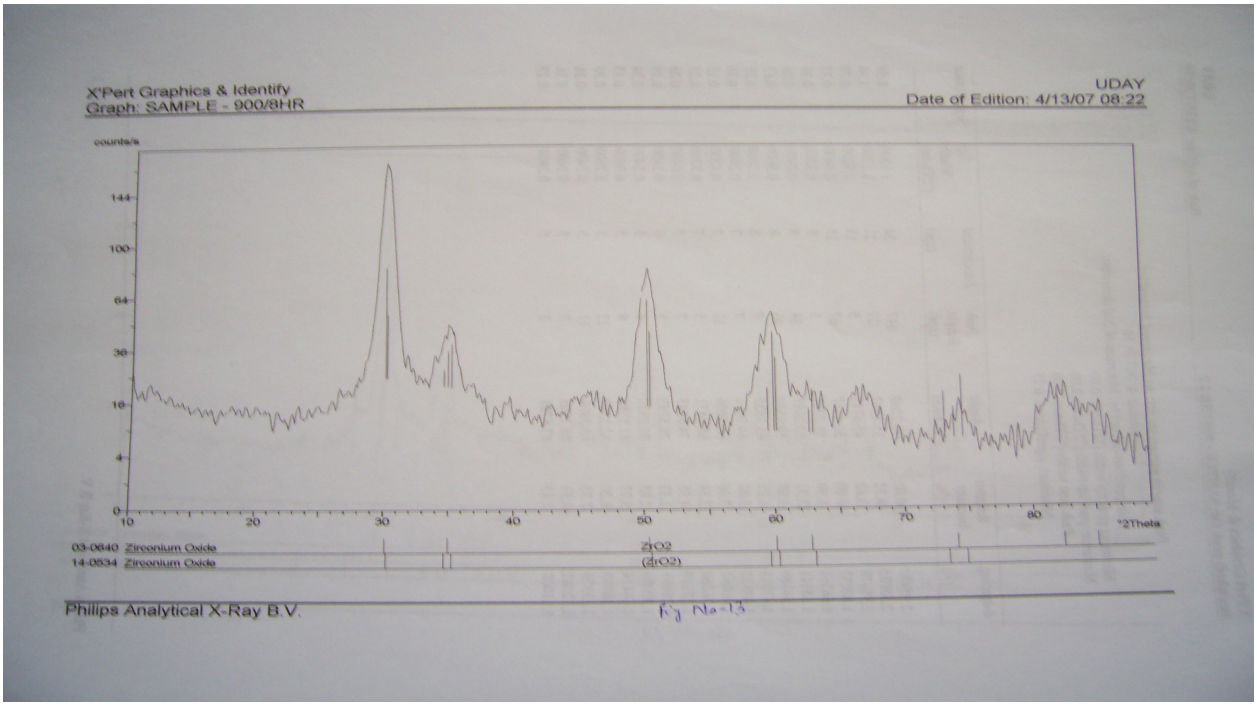
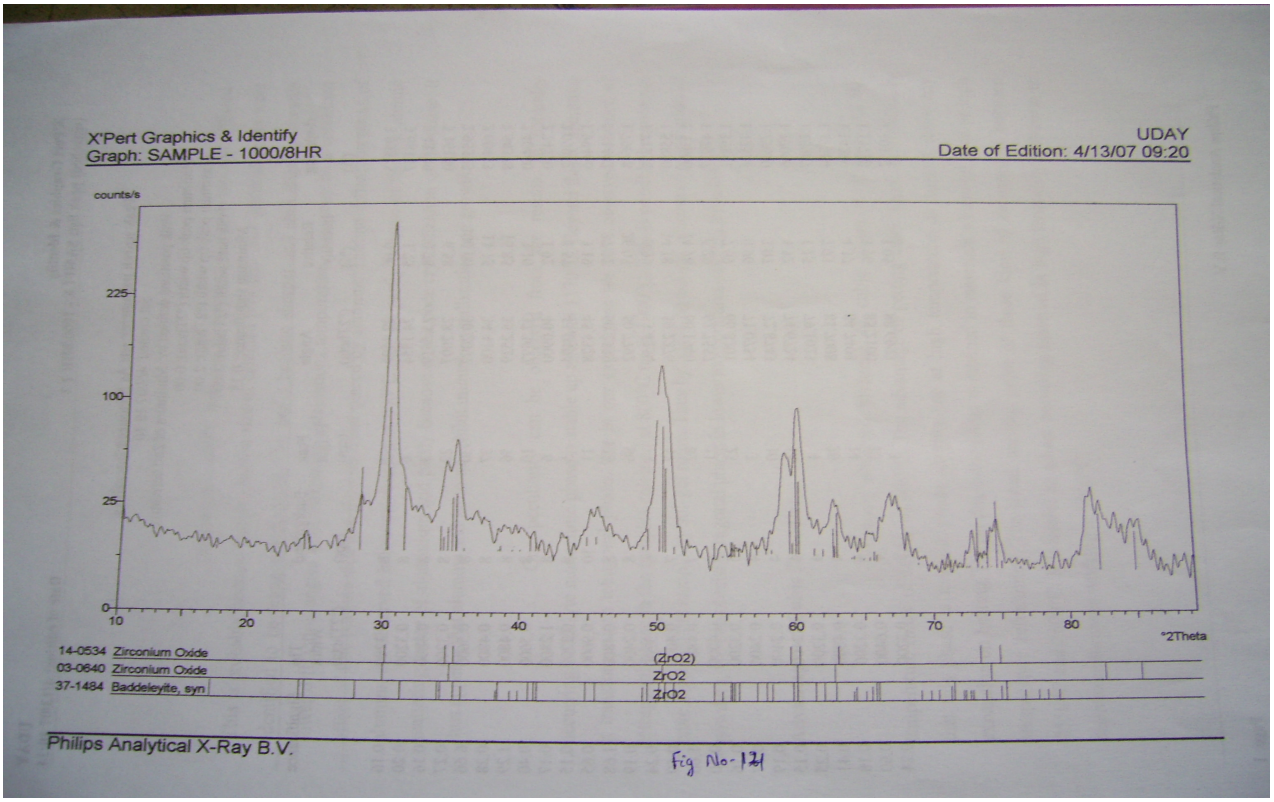


Fig No-13



Diffraction at 900°C indicates that peaks are very broad and diffused. This is probably because fine crystalline size of calcined powders. The diffused peaks were identified to be tetragonal zirconia. The peaks become sharper and shift slightly towards lower diffraction angles with increasing calcinations temperature. This may be a combined effect of fine particle size and the constraint placed by alumina. That no diffraction peaks of alumina are observed below calcination at 900°C may be partly because of the low atomic scattering factor of aluminium and partly because of the poor crystallization of the phase. It thus appears that alumina and zirconia inhibit mutual crystallization and growth.

One peculiarity can be observed from the results. In naturally occurring beddelyte monoclinic phase is stable up to about 1170°C. Beyond this temperature it transforms into tetragonal phase. But in our experiment we have observed presence of tetragonal phase in the samples calcined at 800°C up to 1000°C. This is possible because we have prepared the sample by sol-gel route. Thus by adopting sol-gel process of preparation of powders, we can obtain tetragonal phase in lower temperatures starting from 800°C.

Advantages of Cubic Zirconia:

We have observed presence of cubic phase in samples in the temperature range of 600°C to 800°C. The advantage of getting cubic phase of zirconia is that this phase is a stable phase. During use at high temperatures it doesn't show any expansion on heating. Hence this cubic phase is retained in materials which are used as high temperature refractories. The usual melting point of these kind of ceramics is between 2550°C and 2600°C. It is useful as a heat insulating material in high frequency induction or resistance furnaces working at 2000°C.

Advantages of Tetragonal Zirconia:

In our project work we have observed presence of tetragonal phase of zirconia starting from 800°C up to 1000°C. The advantage of getting tetragonal phase of zirconia in samples is that, during use this tetragonal phase transforms in to monoclinic phase. Due to this transformation micro-pores are generate which subsequently helps in increasing the toughness of the material. This process is known as "Transformation Toughening". Due to this process the toughness of ceramic materials can be improved.

Disadvantages of Monoclinic Zirconia:

In samples calcined beyond 1000°C monoclinic zirconia will be formed. The disadvantage of monoclinic phase of zirconia is that, this phase is very unstable. This monoclinic phase transforms into tetragonal phase which is accompanied with large volume changes which are reversible. On cooling the expansion takes place more rapidly and

suddenly than contraction on heating. Due to these the material cracks and fails. So this monoclinic phase is made stable by adding stabilizers like MgO, CaO or BaO.

CONCLUSION

The following conclusions can be drawn from the present study:

- The presence of cubic phase of zirconia is required in the materials to be used as high temperature refractories. Also in some ceramics tetragonal phase of zirconia is required to increase the toughness of the samples by "Transformation Toughening". The monoclinic phase of zirconia should be made stable by adding stabilizers.

- Since the decomposition reactions are diffusion controlled, long holding time (8 hours) was given for calcination to ensure the completion of all the decomposition reactions.

- Alumina-zirconia composites with varying compositions can also be prepared through this sol-gel route. This method has the advantage that it is simple and of low cost.

- By stabilizing tetragonal phase at lower temperatures transformation toughening can take place in the ceramic matrix. Hence this sol-gel route of preparation is very effective.

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